

Thermostat

Simplest is "constant KE": since $KE = \sum_i \frac{1}{2} m \underline{v}_i^2 = \frac{3}{2} N k_B T$

in equilibrium, at each time step

$$v_{i\alpha} \rightarrow v_{i\alpha} \sqrt{\frac{\frac{3}{2} N k_B T}{KE}} \quad i=1 \dots N, \alpha=1,2,3$$

Not the NVT ensemble however:

should have $p(\underline{v}) = \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-m \underline{v}^2 / 2k_B T}$

$$\Rightarrow \left\langle \sum_i \frac{1}{2} m \underline{v}_i^2 \right\rangle = \frac{3}{2} k_B T \quad \checkmark$$

$$\text{but } \left\langle \left(\sum_i \frac{1}{2} m \underline{v}_i^2 \right)^2 \right\rangle = \frac{15}{4} (k_B T)^2 \neq \left(\frac{3}{2} k_B T \right)^2$$

since fluctuations are absent

Quantitatively,

$$\frac{\overline{(K^2)}}{(\overline{K})^2} = \frac{\overline{(\sum \underline{v}_i^2)^2}}{(\overline{\sum \underline{v}_i^2})^2}$$

$$= \frac{N \langle (\underline{v}^2)^2 \rangle + N(N-1) \langle \underline{v}^2 \rangle^2}{(N \langle \underline{v}^2 \rangle)^2}$$

$$= \frac{2}{3N}$$

or $P_{NVE} \propto e^{-U/k_B T} \delta(K - \frac{3}{2} N k_B T)$

vs $P_{NVT} \propto e^{-H/k_B T} \Big|_K = e^{-U/k_B T} \cdot e^{-K/k_B T} \cdot \frac{1}{k_B T} \left(\frac{K}{k_B T} \right)^{\frac{3N}{2}-1}$

increase
↓

In simulation $\frac{1}{N}$ is not that small, want to do better, or at least allow K to fluctuate

Berendsen Nernst: $m \ddot{r}_i = \underline{F}_i - \zeta \dot{p}_i$ \underline{F} = usual force

$$\zeta = \frac{1}{\tau} \left(1 - \tau / 2k_B / 3N \right) \quad \tau = \text{adjustable relaxation "time"}$$

idea: if K is too small, $\zeta < 0$, positive kick
 K big $\zeta > 0$, negative kick
 similar to deterministic idea

but: wrong fluctuations
 not a Hamiltonian system

Nose-Hoover Nernst: $m \ddot{r}_i = \underline{f}_i - \zeta \dot{p}_i$ again

$$\text{but } \zeta = \frac{1}{\tau} \left(K - \frac{3}{2} N k_B \tau \right) \quad \tau = \text{other relaxation const.}$$

practical advantage:

in Berendsen \underline{p} = deterministic + fluctuating

$$\underline{r} = \int \dot{p} dt \text{ is smoothed}$$

in NIT \dot{p} = deterministic + fluct.

$$\underline{p} = \int \dot{p} dt = \text{smoothed}$$

$$\underline{r} = \int \dot{p} dt = \text{smoother} = \text{better ODF method}$$

And $NVT \leftrightarrow$ real NVT ensemble

derivation in FTS, starts from artificial system where $\{r_i, p_i\}$ coupled to external "bath" variables which are integrated over.

Very roughly speaking

$$H = \sum_i \frac{1}{2} m_i \dot{r}_i^2 + U(\{r_i\}) - \frac{q}{2} \dot{c}^2 - 3NkT \log S$$

Can show ("Lagrangian dynamics") that this system in the NVE ensemble has a partition function (phase space vol)

$\propto Z_{NVT}$. \rightarrow widely used in practice

Other popular choice - Langevin thermostat

$$m\ddot{x} = (F_x) - \underbrace{\gamma \dot{x}}_{\text{friction}} + \underbrace{\eta(t)}_{\text{fluctuation}} \quad \text{in 1-d}$$

originates in Brownian motion widely - particle in fluid sees external forces + "friction + kicks" from fluid molecules; in equilibrium the 2 balance out if γ = right choice

assume fluctuations are random, uncorrelated, zero-mean:

$$\langle \eta(t) \rangle = 0$$

$$\langle \eta(t) \eta(t') \rangle = \alpha \delta(t-t'), \quad \alpha \text{ to be determined}$$

Same "smoothness" property as NH.

Now: look at ICF when $\underline{F} = 0$

later: will show that Langevin solution $\xrightarrow{t \rightarrow \infty}$ canonical ensemble

$$m\dot{v} + \gamma v = e^{-\gamma t/m} \cdot \frac{d}{dt} \left(e^{+\gamma t/m} \cdot m v(t) \right) = \eta(t)$$

$$\Rightarrow e^{\gamma t/m} m v(t) - m v(0) = \int_0^t dt' e^{\gamma t'/m} \eta(t')$$

$$\Rightarrow v(t) = v(0) e^{-\gamma t/m} + \frac{1}{m} \int_0^t dt' e^{-\frac{\gamma}{m}(t-t')} \eta(t')$$

↑
initial velocity is
damped out, time scale $\frac{m}{\gamma}$

↑
integral over past history of η ,
recent times dominate

$\rightarrow v(t) \rightarrow 0 + \text{random fluctuations}$

$$\langle v(t) \rangle = v(0) e^{-\gamma t/m} + \frac{1}{m} \int dt' e^{(\cdot)} \langle \eta(t') \rangle$$

$\xrightarrow{t \rightarrow \infty} 0$

0

$$\langle v^2(t) \rangle = e^{-2\gamma t/m} v^2(0) + 0 +$$

$$+ \frac{1}{m^2} \int_0^t dt' dt'' e^{\frac{\gamma}{m}(2t-t'-t'')} \underbrace{\langle \eta(t') \eta(t'') \rangle}$$

$$= \text{decaying} + \frac{1}{m^2} \int_0^t dt' dt'' e^{\frac{2\gamma}{m}(t-t')} = \frac{d}{dt} \langle v^2(t) \rangle$$

$$= \text{"} + \frac{d}{2m\gamma} \stackrel{\text{should}}{=} \frac{1}{2} kT / \frac{1}{2} m$$

so $\boxed{\alpha = 2\gamma kT}$ Example of the "fluctuation-dissipation" theorem.

$\eta(t)$ $-\gamma v$
 - these must balance in equilibrium.

Use as a thermostat:

need a discrete version to go with ODE solver

continuous $t \rightarrow t_i = i\Delta t$, $x(t) \rightarrow x(i\Delta t) = x_i$

so $\eta(t) \rightarrow \eta_i$, $\langle \eta(t) \rangle = 0 \rightarrow \langle \eta_i \rangle = 0$

$\langle \eta(t)\eta(t') \rangle = \alpha \delta(t-t') \rightarrow \langle \eta_i \eta_j \rangle = \beta \delta_{ij}$

$\beta = ? \int_{t-\tau}^{t+\tau} dt' \langle \eta(t)\eta(t') \rangle = \int_{t-\tau}^{t+\tau} dt' \alpha \delta(t-t') = \alpha$

$\rightarrow \sum_j \Delta t \langle \eta_i \eta_j \rangle = \sum_j \Delta t \cdot \beta \delta_{ij} = \beta \Delta t$

so $\beta = \frac{\alpha}{\Delta t}$, $\eta_i =$ random variable, mean = 0, var. = $\frac{2\gamma kT}{\Delta t}$
 - x -

The MD code uses "ran(x, xx)":

$x = \text{seed} =$ any number in (0,1)

call ran(x, xx) \rightarrow new "random # " xx

$x = xx$

call ran(x, xx) \rightarrow another random xx

"ran" is a minimal grade RNG - doesn't matter for velocity

because MD \rightarrow physics Boltzmann dist with random vel.

Need to fix mean & variance of the random #s:

$\text{ran}(xxx) \rightarrow r$ uniform in $(0,1)$

$u = 2r - 1 \rightarrow u$ " " $(-1,1)$, $p(u) = \begin{cases} \frac{1}{2} & -1 < u < 1 \\ 0 & \text{otherwise} \end{cases}$

$$\text{so } \langle u \rangle = \int_{-1}^1 du p(u) \cdot u = 0$$

$$\langle u^2 \rangle = \int_{-1}^1 du p(u) \cdot u^2 = \frac{1}{3}$$

so $\sqrt{3} \cdot (2r-1) \stackrel{\sim}{=} u$ has mean = 0, variance = 1

The algorithm needs $\tilde{u} * \sqrt{2\gamma kT / \Delta t}$
- x -

Large in Nernst:

use eq brat (const KE) to get to equil at temperature T
then switch to Langevin (or NIT?)

subroutine Langevin

common /vel/ x1(...), y1 ...

for common /force/ fx(...), fy(...)

$$c = \text{sqrt}(6 * \text{gamma} * tr / \text{delta})$$

call ~~ran~~(xxx)

\uparrow "T" in the code

do $i = 1, np$

call ~~ran~~(xxx)

$x = xx$

$$u = c * (2 * x - 1.)$$

$$fx(i) = fx(i) - \text{gamma} * x1(i) + u$$

⋮

This is OK for systems in equilibrium, or at rest.

Moving systems? e.g. a box of ideal gas in a car
 $p + V$ unchanged - same forces, & same dimensions
expect $pV = NkT$ still valid (principle of relativity)
but $\underline{v}_i \rightarrow \underline{v}_i + \underline{v}_{car}$.

→ T represents fluctuations in \underline{v} (fluct. in states, generally)
↔ ability to transfer energy

$$\text{Use } \left\langle \frac{1}{2} m (\underline{v} - \underline{v}_{car})^2 \right\rangle = \frac{3}{2} NkT$$

Systems with internal flow $\langle \underline{v} \rangle \neq 0$:

Assume "local thermodynamic equilibrium" - over regions where

$\underline{v} \approx \text{const}$ we have equilibrium wrt the local avg. \underline{v} .

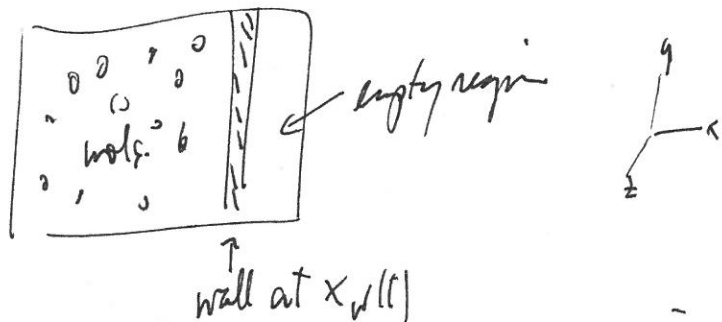
$$\left\langle \frac{1}{2} m (\underline{v} - \langle \underline{v} \rangle_R)^2 \right\rangle = \frac{3}{2} NkT_R \quad R = \text{region}$$

Could have imposed $\langle \underline{v} \rangle$ - moving walls → Couette flow
→ linear profile

or determine $\langle \underline{v} \rangle$ during the calculation + equilibrate
 T about it - "profile-unbiased thermostat".

Pressure control: ("barostat")

1. Simple method, analog of Berendsen thermostat



wall = rigid set of atoms or position of force centers,

$$F_{\text{on } i^{\text{th}} \text{ mol}} = - (x_w - x_i)^{-13} \quad \text{say}$$

$$-\frac{1}{A} \sum_i F_i = \text{pressure exerted on wall by mols.}$$

If desired pressure is p_0 , let $\dot{x}_w = (p - p_0) / \tau$

τ = adjustable parameter, too small - slow relaxation
too big - oscillating wall

(Moving the wall in finite steps \rightarrow big oscillations in p .)

Upside - easy

Downside - not the NpT ensemble
need to relax to desired p

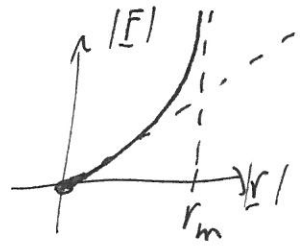
Better - analogs of Nosé-Hoover. See F+S.

Molecules:

single molecules with soft potentials, $U \rightarrow U_{LF} + U_{mol}$

\rightarrow extra terms in $\bar{F} \rightarrow$ new subroutine eval

No other change needed.



Example: polymer melts

use FENE potential $\bar{F} = \frac{-kr}{(1-r^2/r_m^2)}$

k, r_m adjusted to avoid overlap of monomers

Number atoms in molecule 1 = atoms 1, 2, ..., l
 " 2 = l+1, ..., 2l
 etc.

Add

do imol = 1, nmol

do iatom = 1, l-1

$$n1 = (imol-1) * l + iatom$$

$$n2 = n1 + 1$$

$$dx = x(n1) - x(n2)$$

PBC correction

$$dy = \dots$$

$$dz$$

$$fx(i) = fx(i) - dx / (1 - (dx^2 + dy^2 + dz^2) / r_m^2)$$

y

z

enddo

enddo

This assumes $U_{LF} + U_{mol}$ have the same time-step \leftrightarrow similar stiffness

Mix of interactions of different stiffness

- U_{mol} vs. U_{CS} or U_{0-0} vs U_{0-IT} in $\begin{array}{c} H & H \\ | & | \\ H-O-O-H \\ | & | \\ H & H \end{array}$

(recall SHO period = $2\pi \sqrt{\frac{m}{k}}$, $k = \text{stiffness} = V''(\text{min})$,

large $k \rightarrow$ small period \rightarrow small Δt .)

$$\sqrt{V_1''(\text{min})} = m \cdot \sqrt{V_2''(\text{min})} \quad \Delta t_2 = m \Delta t_1$$

VV pseudo code:

do $i=1, n_{\text{step}}$

$$\underline{v} = \underline{v} + \frac{1}{2} m \Delta t \underline{a}_2$$

do $j=1, m$

$$\underline{v} = \underline{v} + \frac{1}{2} \Delta t \underline{a}_1$$

+ \underline{r} updates

recompute \underline{a}_1

$$\underline{v} = \underline{v} + \frac{1}{2} \Delta t \underline{a}_1$$

enddo

~~$\underline{v} = \underline{v} + \Delta t \underline{a}_1$~~ recompute \underline{a}_2

$$\underline{v} = \underline{v} + \frac{1}{2} m \Delta t \cdot \underline{a}_2$$

enddo

— x —

Fully-rigid molecules - treat as classical rigid bodies

Mix of rigid + soft - constraint methods in F&S

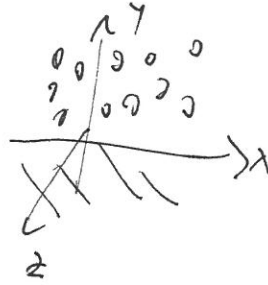
Solid walls

Common MD application is flow in cap. tubes & channels, esp. at $\mu\text{m}/\text{nm}$ scales \rightarrow micro/nano flow problems so need to model the solid wall. In order of realism:

(1) Repulsive potential

e.g. $V_{WF}(y) = V_0 y^{-12}$

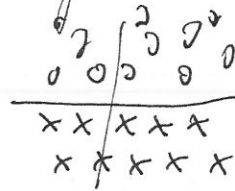
\rightarrow strong repulsion



Keeps liquid out but promotes velocity slip via specular reflection



(2) Fixed atomic lattice



$$V_{FW}(r) = 4\epsilon \left[\left(\frac{r}{\sigma}\right)^{-12} - c \left(\frac{r}{\sigma}\right)^{-6} \right] \quad \text{where } c \leftarrow \text{"chemistry"}$$

- $\left\{ \begin{array}{l} c=1 \text{ slip wall} \\ c=1 \text{ no-slip wall} \\ c < 0 \text{ repulsive wall} \end{array} \right.$

not fully realistic, wall does not respond to liquid

(3) "Tethered" atomic wall - wall atoms have thermal fluctuations

$$V_{FW} \text{ as above} + V_w = \sum_{\underline{r}_w \in \text{wall}} \frac{1}{2} k_w (\underline{r}_w - \underline{r}_{w0})^2$$

\uparrow lattice site

Choose $k_w \ni \Delta r = \sqrt{\langle |\underline{r}_w - \underline{r}_{w0}|^2 \rangle} \lesssim 0.1 \ell$ say

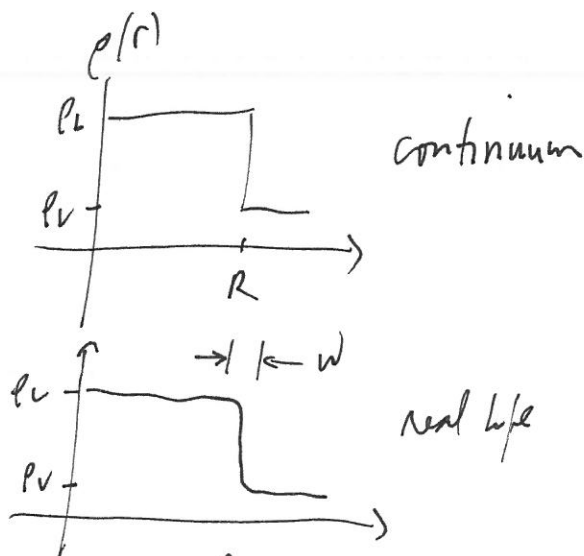
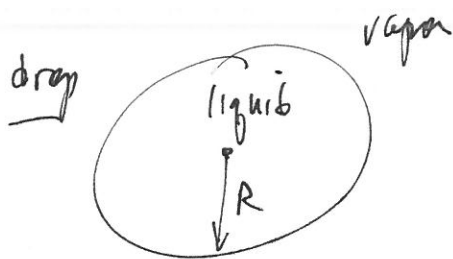
NB - care needed with m_w :

Here $V_w \rightarrow \langle \frac{1}{2} k_w \Delta r^2 \rangle \sim \frac{3}{2} kT$ so $k_w \sim \frac{kT}{(\Delta r)^2} \sim 100$ in MD units

but osc. frequency $\sim \sqrt{\frac{k_w}{m_w}}$ + want this $\gg \frac{1}{\tau}$ to use the same time step as τ (wall dynamics not that important) $\rightarrow m_w \sim 100$.

(a) Realistic wall, modeled as mobile atomic solid

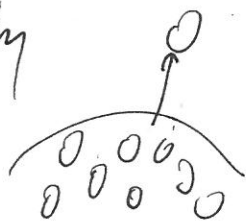
Liquid-vapor interface



good fit is

$$\rho(r) = \rho_v + \frac{\rho_l - \rho_v}{2} \left(1 + \tanh \frac{r-R}{w} \right)$$

molecularly



atom liq \rightarrow vapor

$$\Delta E > 0 \quad \Delta S > 0$$

$$\Delta F = \Delta E - T\Delta S = +a =$$

\rightarrow fluctuating interface

Sketch an interface:

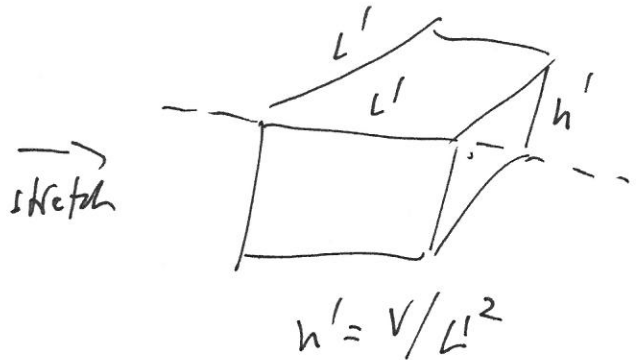
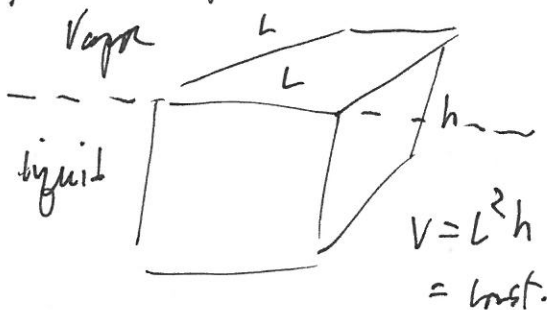
work done
 $\Delta F > 0$



γ arises naturally

write $dF = \gamma dA$ so $\gamma = \left(\frac{\partial F}{\partial A} \right)_{V, T}$

explicit computation:



$$\gamma = \frac{\partial F}{\partial A} = \frac{\partial F}{\partial L} \frac{\partial L}{\partial A} = \frac{1}{2L} \frac{\partial F}{\partial L}$$

$$F = F_{IB} - kT \log \int \prod_i d\mathbf{r}_i e^{-u(\sum_i \mathbf{r}_i^2) / kT}$$

use scaled coordinates $\mathbf{r}_i = (L s_{ix}, L s_{iy}, \frac{\sqrt{V}}{L^2} s_{iz})$

$$= F_{IB} - kT \log \left(V^N \int \prod_i d\mathbf{s}_i e^{-u(\sum_i \mathbf{s}_i^2) / kT} \right)$$

$$\gamma = \frac{1}{2L} \cdot \frac{1}{Q_N} \int V^N \prod_i d\mathbf{s}_i \left(\frac{\partial u}{\partial L} \right) e^{-u/kT} = \frac{1}{2L} \left\langle \frac{\partial u}{\partial L} \right\rangle$$

$$\frac{\partial u}{\partial L} = \frac{\partial}{\partial L} \sum_{ij} u \left(\sqrt{L^2 (s_{ix} - s_{jx})^2 + L^2 (s_{iy} - s_{jy})^2 + \frac{V^2}{L^4} (s_{iz} - s_{jz})^2} \right)$$

$$= \sum_{ij} u'(r_{ij}) \cdot \frac{1}{r_{ij}} \left(L (s_{ix} - s_{jx})^2 + L (s_{iy} - s_{jy})^2 - \frac{2V^2}{L^5} (s_{iz} - s_{jz})^2 \right)$$

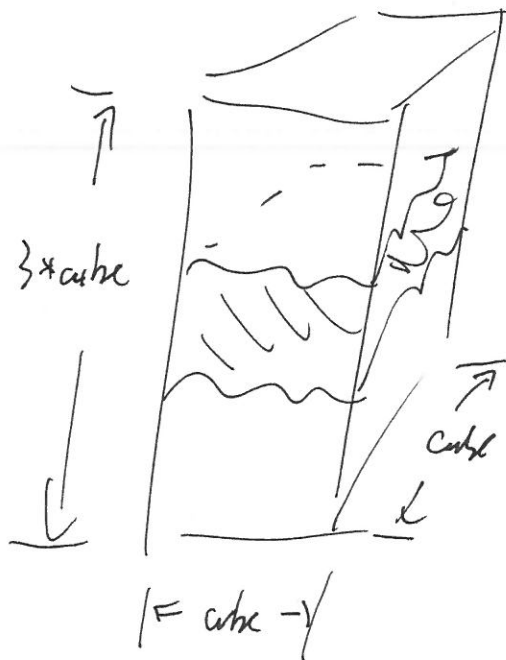
$$= \sum_{i,j} W'(r_{ij}) \frac{1}{r_{ij}} - \frac{1}{L} \left((x_i - x_j)^2 + (y_i - y_j)^2 - 2(z_i - z_j)^2 \right)$$

$$\text{so } \gamma = \frac{1}{2A} \left\langle \sum_{ij} W'(r_{ij}) \frac{r_{ij}^2 - 3z_{ij}^2}{r_{ij}} \right\rangle$$

↑
MC or MD average

Later: relate this to avg over stress differences

Calculation:



Make an initial slab of n_e liquid in substrate free, then let cube \rightarrow 3 * cube in $n_e \geq$ direction & shift n_e atoms to the middle of the cube. After equilibration, compute n_e average above.

To handle the new geometry, look for all occurrences of "cube" in the code, & for those referring to periodic boundaries in z , replace it by $\{ \text{slab} \}$ cube $\} = 3 \times \text{cube}$

- Note 1: $r_{ij}^2 \approx 3z_{ij}^2$ in the bulk liquid, so only the interfacial regions contribute to γ
- 2: Take the average inside substrate eval
 - 3: The absolute position of the slab doesn't matter.